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Final Technical Report

for

AFOSR Grant

FA9550-09-1-0320

Narrow Gap, High Mobility, and Stable Pi Conjugated Polymers

Reporting Period:

May 1, 2009 to April 30, 2012

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(I). Objectives

The development of high mobility and ambient stable, processable π -conjugated and electroactive polymers was carried out for optoelectronic and redox charge storage applications and other devices of interest to the Air Force with a special focus on photodetectors (especially in the near infrared), solar cells, and supercapacitors. Capitalizing on our history of developing variable gap conjugated polymers for a variety of applications (e.g. electrochromism and photovoltaics) we design, synthesize, and characterize polymers having a large enhancement of a property or a high degree of tunability of the property *via* repeat unit, macromolecular structure and morphology. Proto-type devices are developed as platforms for providing feedback on materials properties and for positioning the materials for transition to industrial and Air Force laboratories. Of special note in the polymers proposed is that relatively low HOMO values are targeted for a high degree of ambient (thermo-oxidative) stability, along with ordered structures for high charge mobilities.

(II). Final Program Accomplishment Overview

In the period of 2008-2012, success has been attained in a number of research areas in the frame of high mobility and ambient stable, processable π -conjugated and electroactive polymers for optoelectronic and redox charge storage applications. Of special note through this last grant cycle is the chemistry we have accomplished in developing dithienogermole (DTG) as a new electron donor and isoindigo (iI) as a new electron acceptor and both are becoming ubiquitous building blocks in organic electronic materials across the world. By alternating electron donor (D) and acceptor (A) moieties, new charge transport and solar polymers have been developed. Using dithienosilole (DTS) in conjunction with benzothiadiazole (BTD) as an acceptor, fieldeffect hole mobilities are enhanced by several orders of magnitude, reaching up to 0.1 cm²V⁻¹s⁻¹ with the highest molecular weight fraction of the branched alkyl-substituted polymer derivative in this series. Combining DTG with the thienopyrrolodione (TPD) acceptor has lead to solar polymers that exhibit AM1.5 power conversion efficiencies (PCE) in excess of 8% (7.4%) certified) in collaboration with the group of Prof. Franky So (UF Materials Science and Engineering). Isoindigo has been applied for the first time as an electron acceptor in D-A-D molecular OPV materials and we have elucidated the mechanism of solvent additive enhancement in solar characteristics. Using polydimethylsiloxane (PDMS) as an additive for isoindigo-based molecular OPV, an enhanced PCE in terms of both magnitude and repeatability is observed, which is backed up by reproducible morphologies imaged by AFM and TEM. Finally, isoindigo has been used in a bis-EDOT capped, electropolymerizable D-A-D system to yield highly electroactive films applied in Type I Supercapacitors.

(III). Specific Task Accomplishments

This report serves as a final technical update of the research carried out in the Reynolds research group through funding from the AFOSR from December 1, 2008 to April 30, 2012. It contains progress in seven different technical areas. Following the technical details is a list of personnel supported, publications generated from the grant (32 refereed), presentations at national and international meetings (18) along with research and transition interactions that were carried out.

III-1 Synthetic Cores for Donor-Acceptor Polymer Syntheses

As a baseline in chemistry from this AFOSR project, the Reynolds Research Group has developed chemistry for a variety of electron acceptor (A) and donor (D) moieties that are used in DA polymers as illustrated in Figures 1 and 2. These synthons are used by us, and many others in the field, in developing organic electronic materials. Of special note through this last grant cycle is the chemistry we have accomplished in developing dithienogermole (DTG) as a new electron donor and isoindigo (iI) as a new electron acceptor as both are becoming ubiquitous building blocks in organic electronic materials across the world.

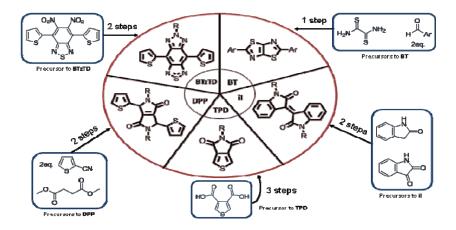


Figure 1. Acceptor type synthons used to prepare D-A polymers

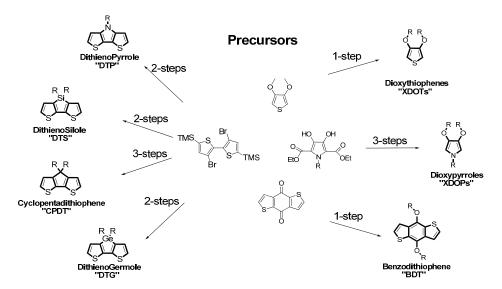


Figure 2. Donor type synthons used to prepare D-A polymers

III-2 Fused Dithienosilole (DTS) as a Donor for High Mobility Polymers

Given the fundamental differences in carrier generation and device operation in organic thin-film transistors (OTFTs) and organic photovoltaic (OPV) devices, the material design principles to apply may be expected to differ. In this respect, designing organic semiconductors that perform effectively in multiple device configurations remains a challenge. Following 'donor-acceptor' principles, we designed and synthesized an analogous series of solution-processable π -conjugated polymers that combine the electron-rich dithienosilole (DTS) moiety, unsubstituted thiophene spacers, and the electron-deficient core 2,1,3-benzothiadiazole (BTD) as illustrated by the structures of Figure 3.

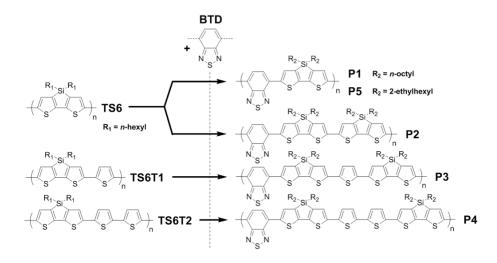


Figure 3. Design principles used for the synthesis of **P1-P5**. On the left: the all-donor **TS6**, **TS6T1**, and **TS6T2** as originally developed by Marks and co-workers for OTFT applications. On the right: derivatization of the **TS6** backbones with the electron-deficient 2,1,3-benzothiadiazole (**BTD**) unit to lead to donor-acceptor repeat unit structures narrowing the polymer optical gap.

Insights into backbone geometry and wave-function delocalization as a function of molecular structure are provided by density functional theory (DFT) calculations at the B3LYP/6-31G** level. Using a combination of X-ray techniques (2D-WAXS and XRD) supported by solid-state NMR (SS-NMR) and atomic force microscopy (AFM), we demonstrate fundamental correlations between the polymer repeat-unit structure, molecular weight distribution, nature of the solubilizing side-chains appended to the backbones, and extent of structural order attainable in p-channel OTFTs. In particular, it is shown that the degree of microstructural order, evident in the 2D-WAXS results of Figure 4, achievable in the self-assembled organic semiconductors increases largely with (i) increasing molecular weight and (ii) appropriate solubilizing-group substitution. The corresponding field-effect hole mobilities are enhanced by several orders of magnitude, reaching up to 0.1 cm²V⁻¹s⁻¹ with the highest molecular weight fraction of the branched alkyl-substituted polymer derivative in this series.

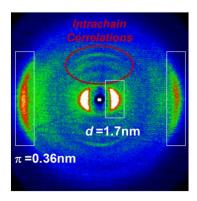


Figure 4. Fiber 2D wide-angle X-ray scattering (2D-WAXS) of **P5.1** (extruded at 210°C).

This trend is reflected in conventional bulk-heterojunction OPV devices as shown in Figure 5 using PC₇₁BM, whereby the active layers exhibit space-charge-limited (SCL) hole mobilities approaching 10⁻³ cm²V⁻¹s⁻¹, and yield improved power conversion efficiencies on the order of 4.6% under AM1.5G solar illumination. Beyond structure-performance correlations, we observe a large dependence of the ionization potentials of the polymers estimated by electrochemical methods on polymer packing, and expect that these empirical results may have important consequences on future material study and device applications.

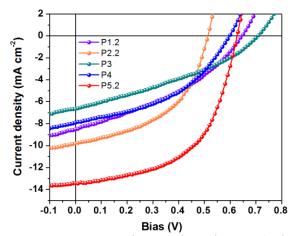


Figure 5. *I-V* curves of **P1.2**, **P2.2**, **P3**, **P4** and **P5.2** –based PSCs (at best polymer:PCBM composition) under AM 1.5 solar illumination, 100 mW cm⁻². Devices with post-polymer processing thermal treatment at 70° C (30 min). The device structure is ITO/PEDOT/PX:PC₇₀BM/LiF/Al with PX = **P1.2**, **P2.2**, **P3**, **P4** or **P5.2**.

III-3 PGREEN Solar Polymer

Using a pentameric oligomer as an oxidatively polymerizable molecule, the polymer PGREEN shown in the reaction below was developed for its green color and ability to be used as the active polymer in PCBM based solar cells.

Simplifying our chemistry, we have developed Stille coupling polymerization methods to produce polymers having the same nominal repeat unit as illustrated by the reaction below.

Polymers of varied molecular weight illustrated in Table 1, such as the M_n = 30.5 kDa (red) and 35.1 kDa (blue) prepared via the Stille method provided effective solar cell results, while retaining the green color of the parent material, when mixed with PCBM.

Table 1. Solar cell results for PGREEN prepared via Stille polymerization

Thickness	I _{SC} (mA/cm²)	V _{oc} (V)	FF (%)	PCE (%)
120 nm	5.82	0.75	46	2.0
135 nm	6.48	0.75	43	2.1
Thickness	I _{SC} (mA/cm ²⁾	V _{oc} (V)	FF (%)	PCE (%)
125 nm	6.46	0.73	0.46	2.19
120 nm	6.27	0.73	0.47	2.14

In collaboration with Prof. Frederik Krebs, fifty large solar cell modules measuring 25 ×25 and comprising 12 serially connected cells were prepared by a combination of slot-die coating and screen printing processing methods. The total active area each of the modules, which only includes the area printed with PGREEN:PCBM, was 450 cm². As such, use of approximately 0.5 grams of a sample PGREEN allowed the printing of 22,500 cm² (2.25 m²) of active solar cell. A photograph of one of the modules is shown in Figure 6, where the module is illuminated on a sunny Florida day and an open circuit voltage of 7.59 V can be observed across the device.



Figure 6. Photograph of a slot-die coated, inverted architecture solar cell module. The photograph was taken on a bright sunny day in Florida.

III-4 Isoindigo as a New Electron Acceptor

Isoindigo has been shown to be a useful electron-accepting unit for the preparation of DA polymers, and DAD molecules as shown by the reaction scheme below.

Using dithienosilole (DTS) as an electron donor in conjunction with isoindigo, the new solar polymer PDTS-iI was prepared and characterized using the reaction chemistry below.

The polymer is broadly absorbing, especially towards the red end of the spectrum as is evident in Figure 7. It can be seen that with an absorption onset near 800 nm and a peak at 720 nm, thin films are able to absorb most of the red light in the visible spectrum while transmitting a substantial amount of blue light. This effect could be important when one considers aesthetically pleasing solar cells such as those developed using PGREEN above.

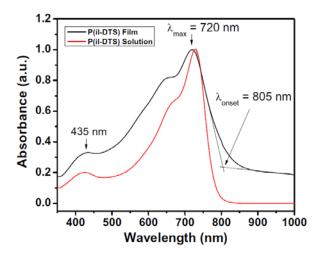


Figure 7. Absorption spectra of **P(DTS-iI)** in solution (red line) and in thin films (black line).

Solar cells investigated the role of various solvent additives with P(DTS-iI) demonstrated that 1,8-diodooctane (DIO) provided the most effective additive as illustrated by the AM1.5 PCE, results along with the AFM and TEM images, shown in Figures 8 and 9. Ultimately, PCEs of 4.0% were attained for this polymer. The effect that DIO has on the morphology of the active material films is evident from the combined transmission electron and atomic force microscopy images. Examining the TEM images shows how overly large domains are converted into a more ordered nanostructure with use of the solvent additive enhancing the solar properties considerably.

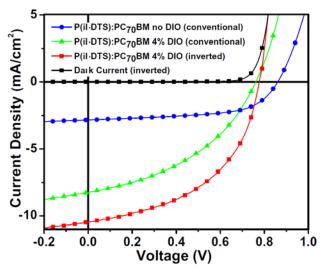


Figure 8. J–V curves of the **P(iI-DTS)**:PC₇₀BM (1:4) based BHJ solar cells with and without DIO additive, under AM1.5 solar illumination, in conventional (blue and green lines) and inverted architecture (red line).

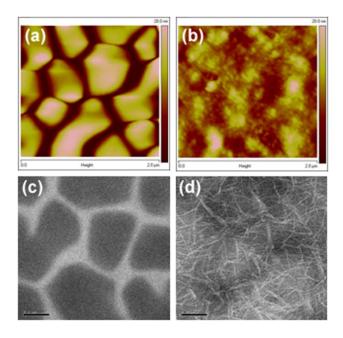


Figure 9. AFM images of the **P(iI-DTS)**:PC₇₀BM blend at 1:4 ratio, processed without (a) and with (b) 4% DIO additive (2 \square m-side, 20 nm-height scales). TEM images of the aforementioned blend, processed without (c) and with (d) 4% DIO additive (200 nm scale bars).

III-5 Solvent Additives in Molecular Bulk Heterojunction Solar Cells

Using a bithiophene capped, isoindigo core, DAD molecule as the donor phase, and PCBM as the acceptor phase, molecular BHJ solar cells were investigated using a broad variety of solvent additives as illustrated by the results of Figure 10. Hansen solubility parameters have been used to indicate which solvent additives are expected to provide the optimal performance.

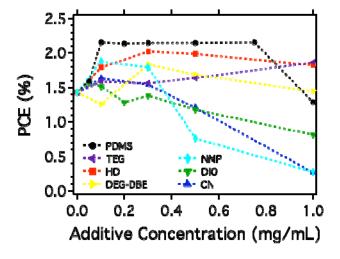


Figure 10. The beneficial effect of solvent additives on the power conversion efficiency of molecular-based solar cells is evident through the use of hexadecanecame (HD) and poly (dimethylsiloxane) (PDMS) with elevated PCE values when 0.1 to 0.8 mg/mL of additive is used.

Due to its poor solvent nature with the TT-iI-TT, poly(dimethylsiloxane) (PDMS) was shown to be the best solvent additive, ultimately yielding high reproducible solar cells results with PCE values of 3.7% as illustrated in Figure 11.

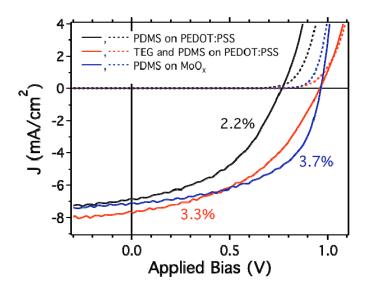


Figure 11. Combining interface control using MoOx as an electron transport material and PDMS as a low vapor pressure solvent additive enhances solar cell efficiencies from less than 2% to 3.7%.

III-6 All Acceptor Conjugated Polymers

Due to its ability to form both brominated and borylated derivatives, polyisoindigo was prepared as a fully electron accepting homopolymer as illustrated by the reactions below. Copolymerization with other acceptor moieties, such as benzothiadiazole shown below, was also accomplished.

Poly(iI) and poly(iI-BTD) demonstrate long wavelength absorbance as desired for organic solar cells as shown in Figure 12. Our discovery that the poly(iI) homo polymer has a long wavelength absorbance beginning at 731 nm and peaks at 690 nm suggests internal donor-acceptor interactions. In addition, the electron affinity makes these polymers especially easy to reduce. These polymers may prove important as electron transport materials in a variety of organic electronic devices.

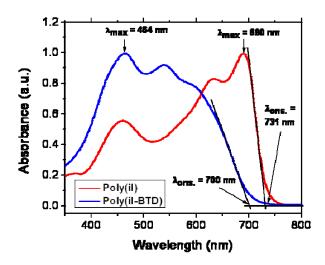


Figure 12. The UV-VIS-NIR spectra of poly(iI) and poly(iI-BTD) demonstrate broad spectral coverage for the alternating copolymer, along with longer wavelength absorbance for the homopolymer, suggesting internal donor-acceptor interactions.

III-7 Dithienogermole (DTG) as a New Electron Donor

New DTG polymers have been prepared with BTD, Pth, and TPD acceptors as illustrated in the reactions below. These polymers have optical absorbances across a broad range of the visible spectra as illustrated by the UV-Vis results in Figure 13.

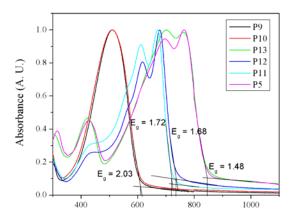


Figure 13. DTG-based polymers show broad spectral coverage controlled by the nature of the acceptor moiety used in the polymerization.

These polymers are high performance solar polymers. PDTG-TPD provides solar cell materials when blended with PCBM that operate in excess of 8% in our laboratory as shown in Figure 14, and have been certified (by Newport) at 7.4%. The device performance of polymer bulk heterojunction (BHJ) solar cells with an inverted geometry has received much attention due to its compatibility with large-scale roll-to-roll (R2R) processing. The inverted cell geometry consists of the following structure: substrate (rigid or flexible)/bottom cathode/electron transporting layer (ETL)/photoactive layer/hole transporting layer (HTL)/top anode. Solution-processed metal oxide films, based on materials such as zinc oxide (ZnO) and titanium oxide (TiO₂), are typically used as ETLs, with ZnO being favored due to its higher electron mobility. The challenge lies in fabricating passivated ZnO nanoparticle films with good size uniformity and spatial distribution of nanoparticles. Here we show enhanced charge collection in inverted polymer solar cells using a UV-ozone treated ZnO-polymer composite as an ETL. Using this approach, inverted polymer solar cells based on the low band-gap polymer having an alternating dithienogermole-thienopyrrolodione repeat unit (PDTG-TPD) with power conversion efficiencies higher than 8% are demonstrated.

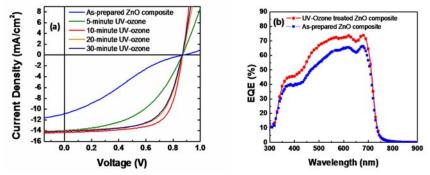


Figure 14. Characterization of inverted PDTG-TPD:PC₇₁BM cells fabricated in our laboratory. (a) Current density versus voltage (*J-V*) curves for devices with either as-prepared or UV-ozone treated ZnO-PVP nanocomposite films as electron transport layers for various treatment times (5, 10, 20, 30 minutes). (b) Corresponding external quantum efficiency (EQE) for the devices with as-prepared and 10-minute UV-ozone treated ZnO-PVP nanocomposite films.

(IV) Personnel Supported with salary:

Principal Investigator:

John Reynolds

Postdoctoral Fellows:

Chad Amb KyuKwan Zong

Graduate Students:

Frank Arroyave Jianguo Mei Pengie Shi Unsal Koldemir

(V) Peer Reviewed Publications that Acknowledge AFOSR During this Period:

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- Steckler, T.T., Zhang, X., Hwang, J., Honeyager, R., Ohira, S., Zhang, X-H., Grant, A., Ellinger, S., Odom, S.A., Seat, D., Tanner, D.B., Rinzler, A.G., Barlow, S., Bredas, J-L., Kippelen, B., Marder, S.R., Reynolds, J.R.

 J. Am. Chem. Soc., 131, 2824-2826 (2009)
 "A Spray Processable, Low Bandgap, and Ambipolar Donor-Acceptor Conjugated Polymer"
- Mei, J., Heston, N.C., Vasilyeva, S.V., Reynolds, J.R.
 Macromolecules, 42, 1482-1487 (2009)
 "A Facile Approach to Defect-free Vinylene-Linked Benzothiadiazole-Thiophene Low-Bandgap Conjugated Polymers for Organic Electronics"
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- Beaujuge, P.M., Pisula, W., Tsao, H.N., Ellinger, S., Mullen, K., Reynolds, J.R. J. Am. Chem. Soc., 131, 7514-7515 (2009)
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 Org. Lett., 12, 660-663 (2010)
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Beaujuge, P.M., Subbiah, J., Choudhury, K., Ellinger, S., McCarley, T., So, F., Reynolds, J.R.,
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 "Green Dioxythiophene-Benzothiadiazole Donor-Acceptor Copolymers for Photovoltaic Device Applications"

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Adv. Mater., 22, 4949-4953 (2010)

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17. Beaujuge, P.M., Amb., C.M., Reynolds, J.R.

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"A Side-Chain Defunctionalization Approach Yields a Polymer Electrochrome Spray-Processable From Water"

18. Beaujuge, P.M., Amb, C., Reynolds, J.R.

Acc. Of Chem. Res., 43, 11, 1396-1407 (2010)

"Spectral Engineering in p-Conjugated Polymers with Intramolecular Donor-Acceptor Interactions"

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23. Amb, C.M., Chen,S., Subbiah,J., Graham, K.R., Small,C.E., So, F., Reynolds, J.R. *J. Am. Chem. Soc.*, **133**, 10062-10065 (2011) "Dithienogermole as a Fused Electron Donor in Bulk Heterojunction Solar Cells"

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"Navigating the Color Palette of Solution Processable Electrochromic Polymers"

28. Dyer, A.L, Thompson, E.J., Reynolds, J.R.

Appl. Mater. Inter., **3**, 1787-1795 (2011)

"Completing the Color Palette with Spray Processable Polymer Electrochromics"

29. Stalder, R., Grand, C., Subbiah, J., So, F., Reynolds, J.R.

Polym. Chem., 3 (1), 89-92 (2012)

"An Isoindigo and Dithieno [3,2-b:2',3'-d]silole Copolymer for Polymer Solar Cells"

30. Small, C.E., Chen, S., Subbiah, J., Amb C.M., Tsang, S.W., Lai, T.H., Reynolds, J.R., So, F.

Nature Photonics, **6** (2), 115-120 (2012)

"High-Efficiency Inverted Dithienogermole-Thienopyrrolodione-Based Polymer Solar Cells"

31. Beaujuge, P.M., Vasilyeva, S.V., Liu, D.Y., Ellinger, S., McCarley, T.D., Reynolds, J.R. *Chem. Mater.*, **24**, 255-268 (2012)

"Structure-Performance Correlations in Spray-Processable Green Dioxythiophene-Benzothiadiazole Donor-Acceptor Polymer Electrochromes"

32. Subbiah, J., Amb, C.M., Irfan, I., Gao, Y., Reynolds, J.R., So, F.

ACS Appl. Mater. Int., 4, 866-870 (2012)

"High-Efficiency Inverted Polymer Solar Cells with Double Interlayer"

Conference Presentations: (presenter underlined when other than John Reynolds)

- 1. F-□-9 International Symposium on Functional □-Electron Systems, Atlanta, GA, May 2010
 - "Aesthetically Pleasing Polymers based on Cyclopentadithiophene for Photovoltaic Applications" with <u>U. Koldemir.</u>
- 2. F-□-9 International Symposium on Functional □-Electron Systems, Atlanta, GA, May 2010
 - "Spanning the Visible Spectrum with Conjugated Electrochromic Polymers" with \underline{A} . Dyer

3. F-□-9 International Symposium on Functional □-Electron Systems, Atlanta, GA, May 2010 "Isoindigo-Based Donor-Acceptor Conjugated Polymers" with R. Stalder. 4. F-□-9 International Symposium on Functional □-Electron Systems, Atlanta, GA, May 2010 "Color Control in Conjugated Polymers for Photovoltaic Applications" with C.M. Amb. 5. FIRST Symposium on Organic Photovoltaics 2010, Kyoto University, Kyoto, Japan, J uly 2010 "Spectral Control with Donor-Acceptor Polymers for Photovoltaics" 6. International Conference on Science and Technology of Synthetic Materials (ICSM), 2010, Kyoto, Japan, July 2010 "Spanning the Spectrum with Donor Acceptor Polymers for Electrochromics and Photovoltaics" 9th International Meeting on Electrochromism (IME-9), Bordeaux, France, September 7 2010 "Spanning the Visible Spectrum with Conjugated Polymer Electrochromics" with A. Dyer, D. Liu. Pacifichem 2010, Honolulu, Hawaii, December 2010 8. "Controlled HOMO-LUMO States in Donor-Acceptor Pi-Conjugated Polymers for Nanostructured Photovoltaics". 9. ACS Spring National Meeting, Anaheim, CA, March 2011 "Extending pi conjugated systems for optoelectronic and redox function" 10. MRS Spring National Meeting, San Francisco, CA, April 2011 "Completing the Color Palette with Conjugated Electrochromic Polymers" with A. Dyer. C. Amb, D. Liu, M. Craig, E. Thompson, E. Knott, J. Kerszulis, A. Chilton, J. Babiarz FAME, 14th Organic IV COPE Scholar Symposium, Tampa, FL, May 2011 "Spanning the Spectrum with Donor-Acceptor Polymers for Electrochromics and Photovoltaics" 12. 14th International Symposium on Novel Aromatic Compounds, Eugene, OR, July 2011 "Synthesis of 3,4-Dioxypyrroles (XDOPS) as Molecular Synthons for Electroactive Polymers" with F. Arroyave 13. F-□-10 International Symposium on Functional □-Electron Systems, Beijing, China, October 2011 "Conjugated Donor-Acceptor Systems: Pushing the Limits Using Chemistry"

- 14. Materials Research Society Fall National Meeting, Boston, MA, Nov 2011 "High Efficiency Dithienogermole as a Fused Electron Donor in Bulk Heterojunction Solar Cells" with <u>C. Small</u>, C. Amb, S. Chen, K. Graham, J. Subbiah, F. So
- 15. Materials Research Society Fall National Meeting, Boston, MA, Nov 2011 "Achieving Higher than 8% Power Conversion Efficiency by Modified Electron Extraction Layer in Polymer Bulk Heterojunction Solar Cells" with <u>S. Chen</u>, C. Small, C. Amb, T. Lai, K. Graham, F. So
- 16. Materials Research Society Fall National Meeting, Boston, MA, Nov 2011 "Isoindigo, a Versatile electron-Deficient Building Block in p- and n- type Conjugated Systems" with R. Stalder, J. Mei, K. Graham, C. Grand, L. Estrada, J. Subbiah, F. So
- 17. Florida Energy Systems Consortium, Gainesville, FL, February 2012 "Efficient Inverted Polymer Solar Cells using Silole-containing low-bandgap polymer" with C. Small, F. So.
- 18. Materials Research Society Spring National Meeting, San Francisco, CA, April 2012. "Conjugated Molecules and Polymers for Energy Conversion and Storage: Pushing the Limits Using Chemistry."

(VI) INTERACTIONS AND TRANSITIONS

An important element of our research effort has been to develop external collaborations and interactions with government, industrial, and other academic researchers in order to more fully explore the properties of our conducting and electroactive polymers and to develop possible applications. As our research has led to the development of a broad family of new systems, they have generated significant interest from outside laboratories. We are utilizing five external interactions detailed below as routes with which to attain a higher level of materials properties characterization, along with device construction and testing. The Reynolds group has formed important liaisons with multiple companies that impact this work through collaboration or materials development for commercialization.

Present collaborations interactions and transitions:

1. BASF. We continue our active collaboration with BASF (in the past known as Ciba Specialty Chemicals) in developing electroactive and electronic materials. BASF is now sampling a number of our electrochromics polymers (being prepared up to 100 gram scale), to multiple potential customers.

- **2. Nanoholdings/nRadiance LLC.** The University of Florida and Nanoholdings Inc. has established a start-up company, nRadiance Inc., to develop technology coupling transparent carbon nanotube films with our electroactive polymers and devices. Nanoholdings continues their support of the Reynolds Research Group at Geaorgia Tech as we develop new compositions of nanotube inks for printing and spraying.
- **3. Professor Franky So (University of Florida).** The Reynolds and So groups meet regularly in so-called "SoRey Team Meetings" in Tifton Georgia to collaborate in the area of polymer solar cells.
- **4. AFRL.** The Reynolds group is participating in a joint program with Dr. Michael Durstock investigating the utility of conjugated polymers and hybrid composite materials in flexible batteries
- **5. Professor Bernard Kippelen (Georgia Tech)**. The Reynolds group collaborates with the Kippelen group who utilize our molecular materials in a combination of solar cells and FETs.

(VII) Awards and Honors received by the PI (life-time received):

- 1. University of Florida, Research Foundation Fellowship 1999
- 2. V.T. and Louise Jackson Professor of Chemistry, University of Florida, College of Liberal Arts and Sciences, 2008
- 3. Term Professor, Colonel Allan R. and Margaret C. Crowe Professorship, University of Florida, College of Liberal Arts and Sciences, 2008
- 4. American Chemical Society, ACS Award in Applied Polymer Science 2012